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RESEARCH MEMORANDUM

PHYSICAL AND CHEMICAL PROPERTIES OF HEF-2 (NACA FUEL 56Z4)

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RESEARCH MEMORANDUM

PHYSICAL AND CHEMICAL PROPERTIES OF HEF-2 (NACA FUEL 56Z4)

By A. E. Spakowski, P. O'Donnell, and M. Buddie

4393

SUMMARY

The following chemical and physical properties of HEF-2 were measured:

Elemental analysis, percent by weight:	
Boron	47.73
Carbon	36.63
Hydrogen	15.96
Net heat of combustion of liquid fuel to gaseous carbon dioxide and water, and solid boric oxide at 25° C, Btu/lb	-23,974
Density, g/ml at:	
-40° C	0.7469
0° C	0.7204
20° C	0.7083
25° C	0.7050
Freezing point, °C	-125
Self-ignition temperature, °C	109
Flash point, °C	-13
Viscosity, centistokes at:	
-40° C	3.234
0° C	1.672
38° C	0.950
Molecular weight	101
Water stability:	
Initial reaction rate, (ml/min)/g BCF	485
Initial reaction time, min	4
Vapor pressure at 25° C, mm	43.7
Extrapolated boiling point, °C	129
Heat of vaporization, cal	6519.1
Refractive index at 25° C	1.4542

The oxygen stability of this fuel was also determined.

[redacted]

INTRODUCTION

As part of Project Zip to screen various boron-containing materials as potential high-energy fuels, the chemical and physical properties of the high-energy fuel HEF-2 (NACA fuel 56Z4) prepared by Olin Mathieson Chemical Corporation were evaluated at the NACA Lewis laboratory. The properties measured included elemental analysis, heat of combustion, density, freezing point, self-ignition temperature, flash point, viscosity, molecular weight, vapor pressure, refractive index, and the water and oxygen stability. The analytical test methods employed for these determinations are those adopted by the Project Zip Standard Specifications Committee.

PROCEDURE AND RESULTS

Chemical analysis. - The sample of propylpentaborane fuel (NACA fuel 56Z4) was received in a steel bomb under an atmosphere of dry nitrogen and was later transferred into a smaller steel bomb that was stored in a dry box inerted with prepurified nitrogen. All analytical samples were handled in the dry box to ensure against any oxidation prior to the analysis. The fuel was a clear, light amber liquid.

The elemental analysis for boron, carbon, and hydrogen in HEF-2 followed the methods set up by the Project Zip Standard Specifications Committee (ref. 1). Boron was determined by the nitric acid oxidation method, and was found to be 47.73 percent by weight. By using the microcombustion technique, 36.63 and 15.96 percent by weight of carbon and hydrogen, respectively, were present in HEF-2. These data together with the remainder of the analytical results discussed in the following paragraphs are tabulated in table I.

Heat of combustion. - A standard Parr adiabatic oxygen-bomb calorimeter and the method as described in reference 1 were used to determine the heat of combustion of HEF-2. The most recently approved modification to the method, that of increasing the initial oxygen pressure from 30 to 40 atmospheres, was used. The results from six determinations are listed in table II, together with the corrections made to the raw heat values. From the analysis of the combustion products, the average combustion efficiencies for boron and carbon using 40 atmospheres of oxygen approach 85 and 91 percent, respectively. The combustion of the hydrogen is assumed to be complete. The average net heat of combustion of HEF-2 was -23,974 Btu per pound based on a reference temperature of 25° C and liquid fuel going to gaseous carbon dioxide and water, and solid boric oxide.

Density. - The density was determined in an open-arm bicapillary pycnometer whose arms were connected by a nitrogen filled tube at atmospheric pressure in order to seal the sample from the possibility of air oxidation. The pycnometer was filled with the sample in the dry box, and the measurements were taken in the usual manner. The densities recorded were 0.7469, 0.7204, 0.7083, and 0.7050 gram per milliliter, at -40°, 0°, 20°, and 25° C, respectively. The variation of density over the temperature range from -40° to 25° C is shown plotted in figure 1, and is represented by the equation

$$d = 0.7212 - 0.000645\ t$$

where d is the density (g/ml), and t is the temperature (°C)

4393

Freezing point. - The freezing point of HEF-2 was measured in an apparatus with a motor-driven reciprocating stirrer and a thermocouple-potentiometer system to record the temperature. As a sample of HEF-2 was cooled in a liquid-nitrogen bath, its viscosity increased markedly, but the fuel remained clear. At -113° C white crystals appeared and formed a slush with the remaining liquid. When the temperature was subsequently lowered to -125° C, the mass became solid.

Self-ignition temperature. - The self-ignition temperature was determined in the Setchkin apparatus (refs. 1 and 2). The usual procedure was followed wherein ignition attempts were made as the temperature was lowered with the same flask being used without cleaning, but with thorough flushing between ignitions. When the lowest ignition temperature was found, the value was repeatedly checked using a series of clean flasks. The self-ignition temperature obtained was 109° C. During the ignition studies of HEF-2, all the ignition delays were of the order of 2 seconds or less.

Flash point. - The flash point was measured in a Tag closed-cup flash-point tester using a modified cup (unpublished data). The main advantage of the new cup (illustrated in fig. 2) is the reduction of sample size from 50 to 1 cubic centimeter. It will be noted that the modified cup is a duplicate of the ASTM cup with the exception that the depth has been decreased and a depression made in the bottom. The procedure in determining the flash point of the liquid HEF-2 follows that detailed in ASTM method D56-52 (ref. 3). The temperature rise of the cup was held to less than 1° C per minute. The flash points measured for two runs were -12° and -13° C.

Viscosity. - A Cannon-Manning semimicro viscometer was used to measure the viscosity of HEF-2 over a range of temperatures. An adapter was made for the viscometer, which made it possible to keep the viscometer filled with an inert atmosphere (prepurified nitrogen) during the determination, and also could be used to manipulate the fuel sample for repeat runs. The viscosities measured at -40°, 0°, and 38° C were 3.234, 1.672, and 0.950 centistokes, respectively. The equation relating the change of viscosity to the temperature over the range studied is given by the following equation:

$$\log \eta = -1.434 + \frac{452.8}{T} + \frac{275}{T^2}$$

where η is the viscosity (centistokes) and T is the temperature ($^{\circ}$K). 4393

Molecular weight. - The molecular weight of HEF-2 was estimated by the freezing-point-lowering technique with benzene as the solvent. The molecular weight determined was 101.

Water stability. - The water stability of HEF-2 was determined in a homogeneous system currently under study at the Lewis laboratory. The object of the experiment was to measure the rate at which gas was liberated in a closed homogeneous system when water and the fuel sample are mixed with a common solvent under specified conditions. The common solvent is used to remove the unknown variable of the contact area between the fuel and water by making contact on a molecular scale possible. The standard test apparatus is shown in figure 3. It consisted of a 100-milliliter round-bottom flask and a 100-milliliter gas buret in a constant-temperature air bath controlled at 86° F. During an initial run, it was discovered that the liberation of hydrogen was so rapid at the beginning of the run that the gas buret could not be used effectively. A wet-test meter was added to measure this initial evolution of gas. The reaction flask had a sidearm fitted with a rubber-serum cap through which the fuel sample was admitted with a hypodermic needle and syringe.

At the start of the hydrolysis test, 5 milliliters of water and 25 milliliters of dioxane were added to the round-bottom flask and brought to the test temperature of 86° F. The wet-test meter and the gas buret were set to zero, and the three-way stopcock turned to equalize the pressure inside the flask. The constant-temperature bath contained air, but any inert gas, that is, nitrogen, could be substituted, or, just the apparatus itself could be inerted. This action would depend, of course, upon the reactivity of the fuel with the oxygen and water present in the air. After the water-dioxane mixture had attained the test temperature, a weighed sample of HEF-2 was added to the flask by means of a 1-milliliter syringe. The volume of gas generated was recorded as a function of time. The results are shown in figure 4 where the accumulative volume of gas liberated is plotted against the time in hours. The initial reaction rate was 485 milliliters per minute per gram of fuel, and the reaction ceased in slightly more than 5 hours. The gas liberated was analyzed by gas chromatography and found to be pure hydrogen. No evidence of propane was found in either of two gas samples, although the method could detect less than 0.1 percent propane.

Vapor pressure. - The vapor pressure of HEF-2 was determined in an isoteniscope. The standard procedure adopted by Project Zip was followed throughout (ref. 1). Prior to adding the sample, the isoteniscope was degassed and then filled with dry, prepurified nitrogen. The sample of HEF-2 was added and degassed, and then the sealed isoteniscope was placed in a clear mineral oil bath. Vapor pressure measurements were made over the temperature range of 23.5° to 76.5° C; the temperature 76.5° C was dictated by the limited manometer range of the isoteniscope.

4393 The results are shown in figure 5, where the logarithm of the pressure in millimeters of mercury is plotted against the reciprocal of the absolute temperature. The straight-line curve over the temperature range covered can be represented by the equation

$$\log P = \frac{6519.1}{-2.303\ RT} + 6.4203$$

where P is the pressure (mm of Hg), T is the temperature (°K), and R is the gas constant (1.987). The mean molar heat of vaporization over the temperature range covered is 6519.1 calories. By extrapolating the straight-line vapor-pressure curve to a pressure of 760 millimeters, a boiling point of 129° C was obtained.

Refractive index. - The refractive index of HEF-2 was determined on an Abbé refractometer at 25° C to be 1.4542.

Oxygen stability. - The oxygen stability of HEF-2 was determined in the apparatus used for the water stability test at a constant temperature of 30° C. The apparatus was thoroughly cleaned, dried, and then filled with enough pure oxygen so that the volume decrease could be followed with the gas buret. Five milliliters of fuel was added to the flask through the rubber-serum cap by means of a hypodermic needle and syringe. The total-volume change of the system was recorded as a function of time.

In figure 6 the volume decrease of the system is plotted against the time in hours. The following table expresses the volume changes in terms of a rate per unit of time:

Type of volume change	Rate of volume change, ml/hr	Time interval, hr
Decrease	4.5	0 - 8
Decrease	.165	8 - 170
Increase	.015	170 - 292

As the test progressed, the sample became increasingly viscous while retaining its original clear, light amber appearance. The results are difficult to interpret with the limited amount of information obtained. Unknown factors include the chemical nature of the viscous end product and the volume of oxygen consumed, as well as, the amount of other gases liberated during the slow reaction. 4393

DISCUSSION

The experimentally determined heat of combustion of HEF-2 was -23,974 Btu per pound, which represents approximately 29 percent more heat than is available in hydrocarbon fuels. Based on an estimate of its composition by mass spectrometry (information received from Olin-Mathieson Chemical Corp.), a heating value of -24,700 Btu per pound was calculated for HEF-2 following the method of reference 4. For comparison to this theoretical value, a heat of combustion of -24,770 Btu per pound was calculated from the actual elemental analysis using an atomic-bond energy method (ref. 5).

The low viscosity of HEF-2, especially noticeable at the lower temperatures, almost eliminates the low-temperature handling problems usually associated with other chemical fuels, that is, the ethyldecaborane types. On the other hand, this advantage may be more than offset by the high vapor pressure exhibited by HEF-2. For any high-temperature applications, this high vapor pressure must be given a more thorough study as must its thermal stability and any relations that may exist between the two.

It was shown in the oxygen and water stability tests that HEF-2 was quite reactive with elements from its natural environment, to what extent is more easily seen by comparison with a chemical fuel of the ethyldecaborane type. HEF-3 was chosen as the standard in this instance as it represents one of the more stable commercial fuels of this class. The oxygen stability of HEF-2 is graphically compared with HEF-3 in figure 6, where the volume (oxygen) decrease is plotted against the time in hours. Both fuels were tested in similar apparatus at approximately the same temperature (30° C). The plot may be interpreted to mean that HEF-2 is considerably more unstable in the presence of oxygen. If it is assumed that the volume decrease of the system mainly represents the reaction of oxygen and fuel to form a solid product, the HEF-2 would be considerably more reactive in air.

HEF-3 was again used as the standard of comparison for the water stability of HEF-2. In the following table several parameters are listed which indicate the degree of reactivity of each fuel in a homogeneous fuel-water system:

Fuel	Initial reaction time	Initial reaction rate	
		(ml H_2/hr)/g BCF	moles H_2/mole BCF
HEF-2	4 min	29,100	5.25
HEF-3	3 hr	54	1.09

4393

These data point out the fact that HEF-2 is extremely reactive with water and that a large volume of gas can be released in a short period of time.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, February 7, 1957

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4393

TABLE I. - CHEMICAL AND PHYSICAL PROPERTIES OF HEF-2 (NACA FUEL 56Z4)

Elemental analysis:	
Boron, percent	47.73
Carbon, percent	36.63
Hydrogen, percent	15.96
Heat of combustion at 25° C, Btu/lb	-23,974 (at 25° C)
Density, g/ml at:	
-40° C	0.7469
0° C	0.7204
20° C	0.7083
25° C	0.7050
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Flash point, °C	-13
Viscosity, centistokes at:	
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38° C	0.950
Molecular weight	101
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Initial reaction time, min	4
Vapor pressure, mm	43.7 at 25° C
Boiling point (extrapolated), °C	129
Heat of vaporization, cal	6519.1
Refractive index, 25° C	1.4542
Density equation, -40° to 25° C	$d = 0.7212 - 0.000645\ t$
Viscosity equation, -40° to 38° C	$\log \eta = -1.434 + \frac{452.8}{T} + \frac{275}{T^2}$
Vapor pressure equation, 23.5° to 76.5° C	$\log P = -\frac{6519.1}{2.303\ RT} + 6.4203$

TABLE II. - HEAT OF COMBUSTION OF HEF-2

	Determination					
	1	2	3	4	5	6
Sample weight, g	0.1800	0.1380	0.6388	0.7150	0.5496	0.4822
Bomb pressure, atm	30	30	40	40	40	40
Boron burned, percent	56.7	76.7	85.6	81.5	86.0	83.8
Carbon burned, percent	76.5	80.5	90.6	89.4	90.9	91.9
Raw heat, Btu/lb	-18,921.3	-21,523.4	-23,719.4	-23,333.7	-23.450.1	-23,290.1
Corrections, cal/g:						
To atmospheric pressure for oxygen consumed	-2.4	-2.7	-3.9	-3.8	-3.9	-3.8
Constant volume to constant pressure	-31.9	-35.8	-37.7	-36.8	-37.9	-37.4
Hydration solution of boron oxide	205.8	277.7	355.2	327.4	346.8	335.5
Vaporization of water	736.4	736.4	736.4	736.4	736.4	736.4
Unburned boron	-2,957.2	-1,659.6	-980.7	-1,282.4	-950.5	-1,101.4
Unburned carbon	-701.2	-613.6	-282.4	-321.4	-272.7	-243.5
Total corrections:						
cal/g	-2750.5	-1,297.6	-213.1	-580.6	-181.8	-314.2
Btu/lb	-4950.9	-2,335.7	-383.6	-1,045.1	-327.2	-565.6
Neat heat of combustion, Btu/lb	-23,872.4	-23,859.1	-24,103.0	-24,378.8	-23,777.3	-23,855.7
Average neat heat of combustion				-23,974.4		

4393

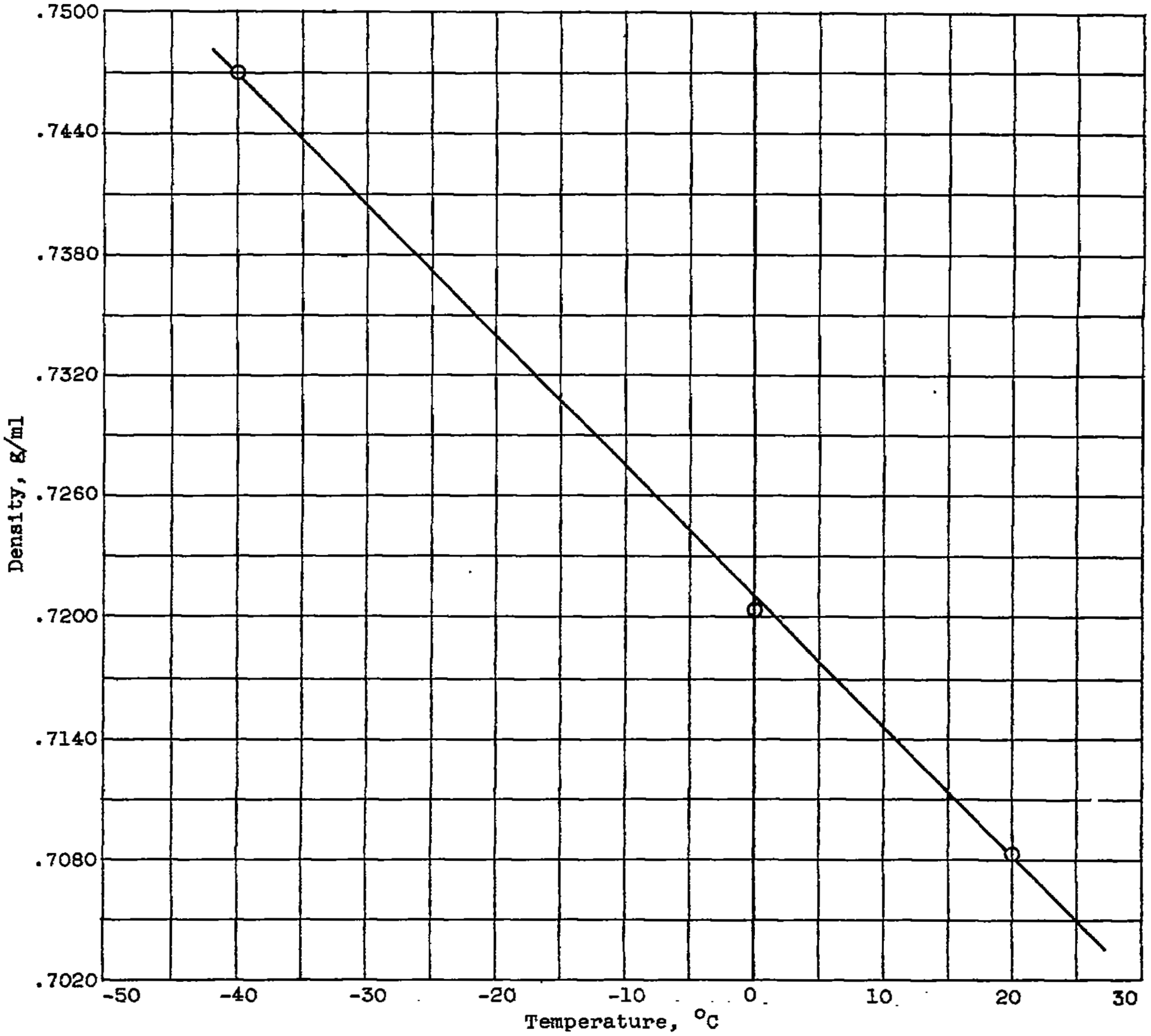

Figure 1. - Density change of HEF-2 with temperature increase.

4393

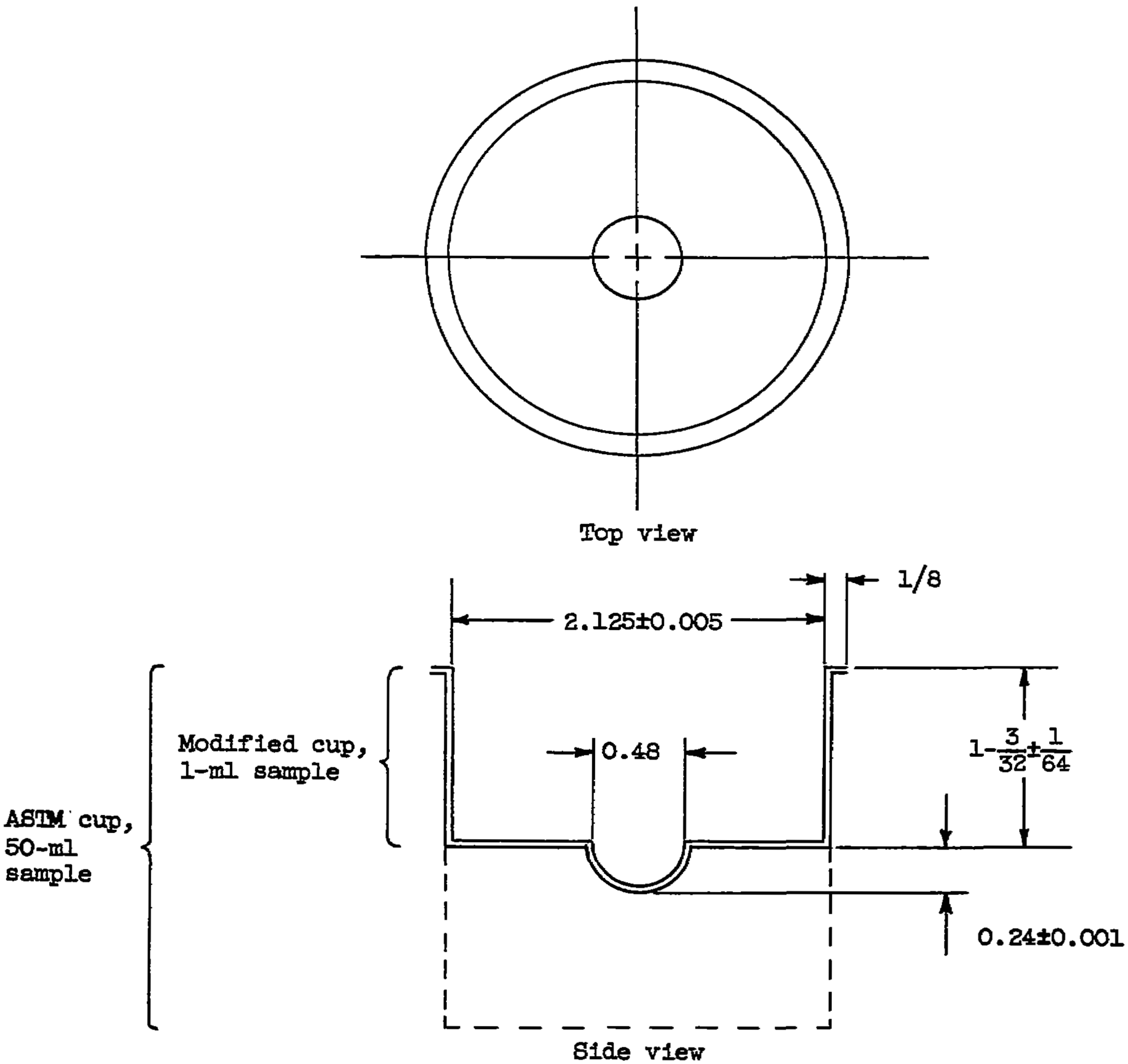

Figure 2. - Comparison of modified flash-point cup with standard ASTM flash-point cup. Material, 1/32-inch sheet brass. (All dimensions are in inches.)

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4398

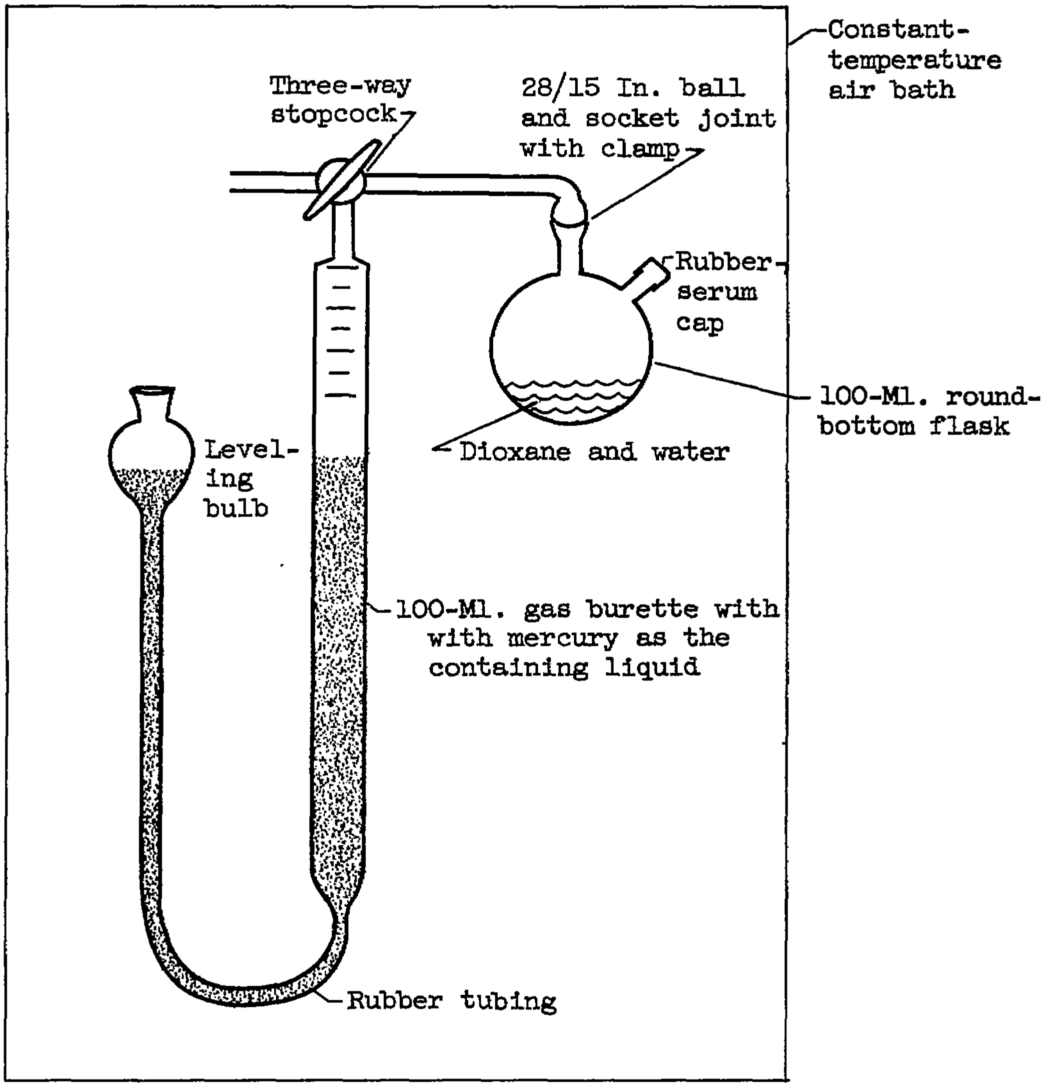

Figure 3. - Test apparatus for water hydrolysis of boron-carbon-hydrogen fuels in a homogeneous system.

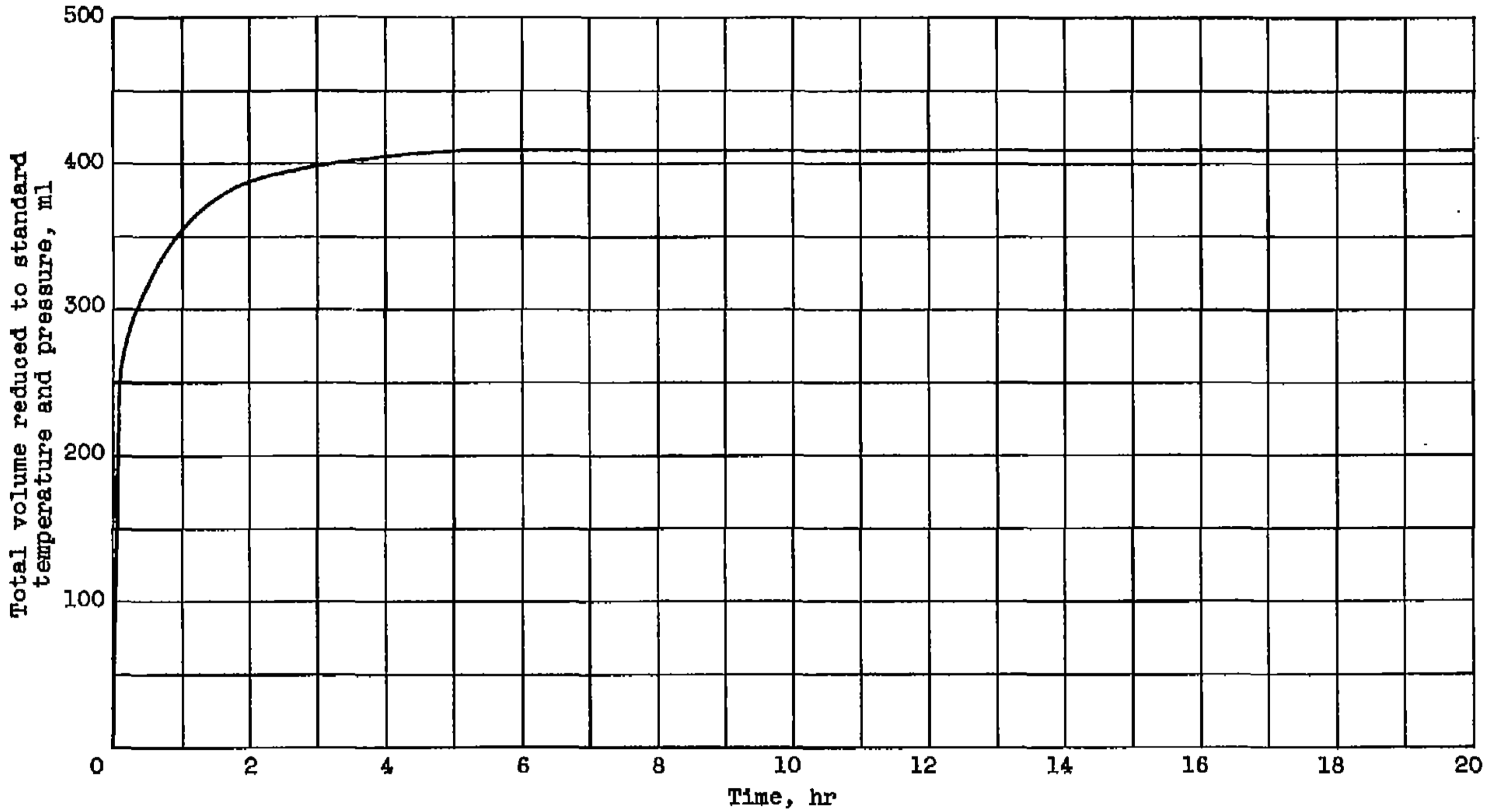

Figure 4. - Reaction of HEF-2 with water in a homogeneous system at 30° C with a HEF-2 weighted sample of 0.2063 gram.

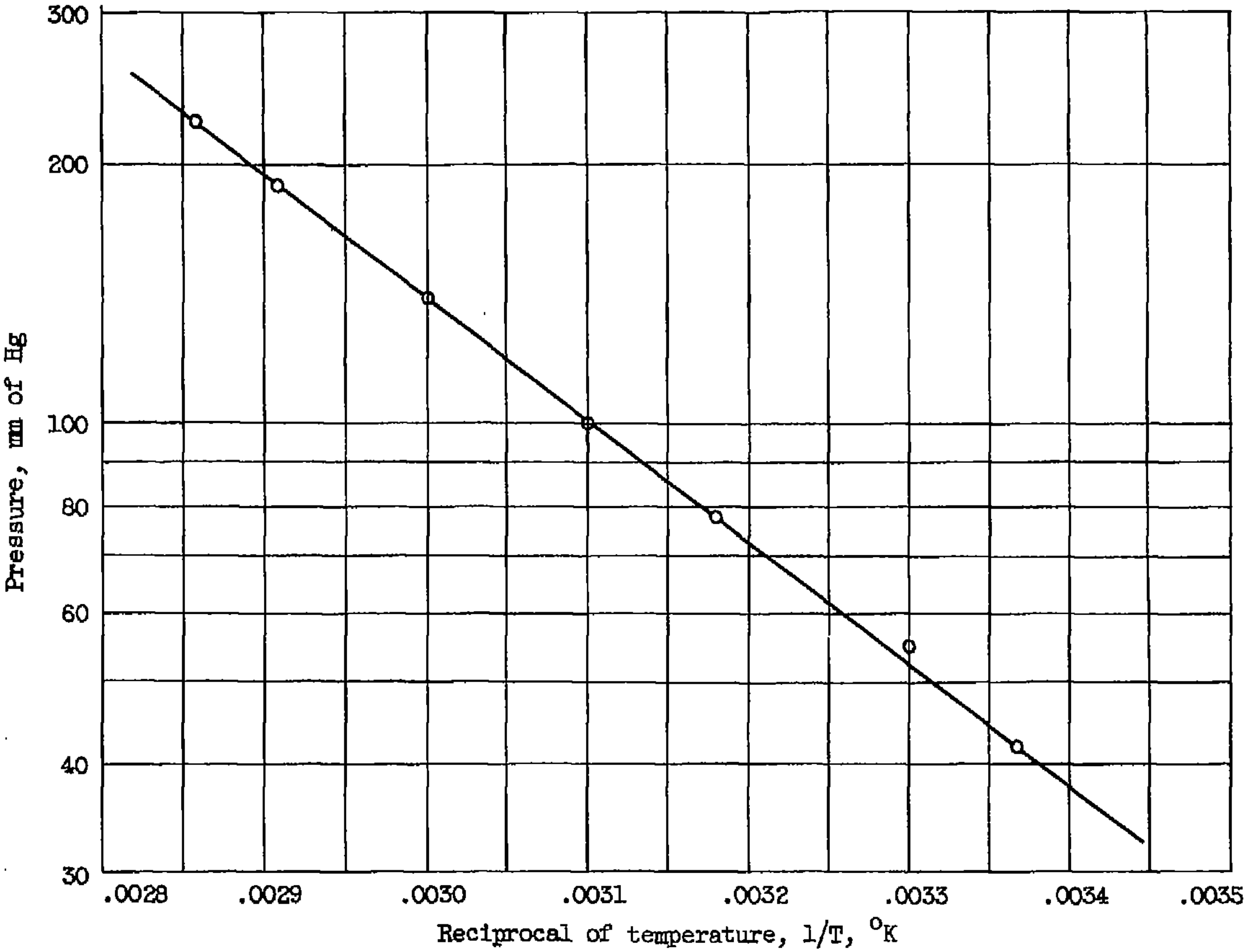

Figure 5. - Vapor pressure - temperature relation of HEF-2.

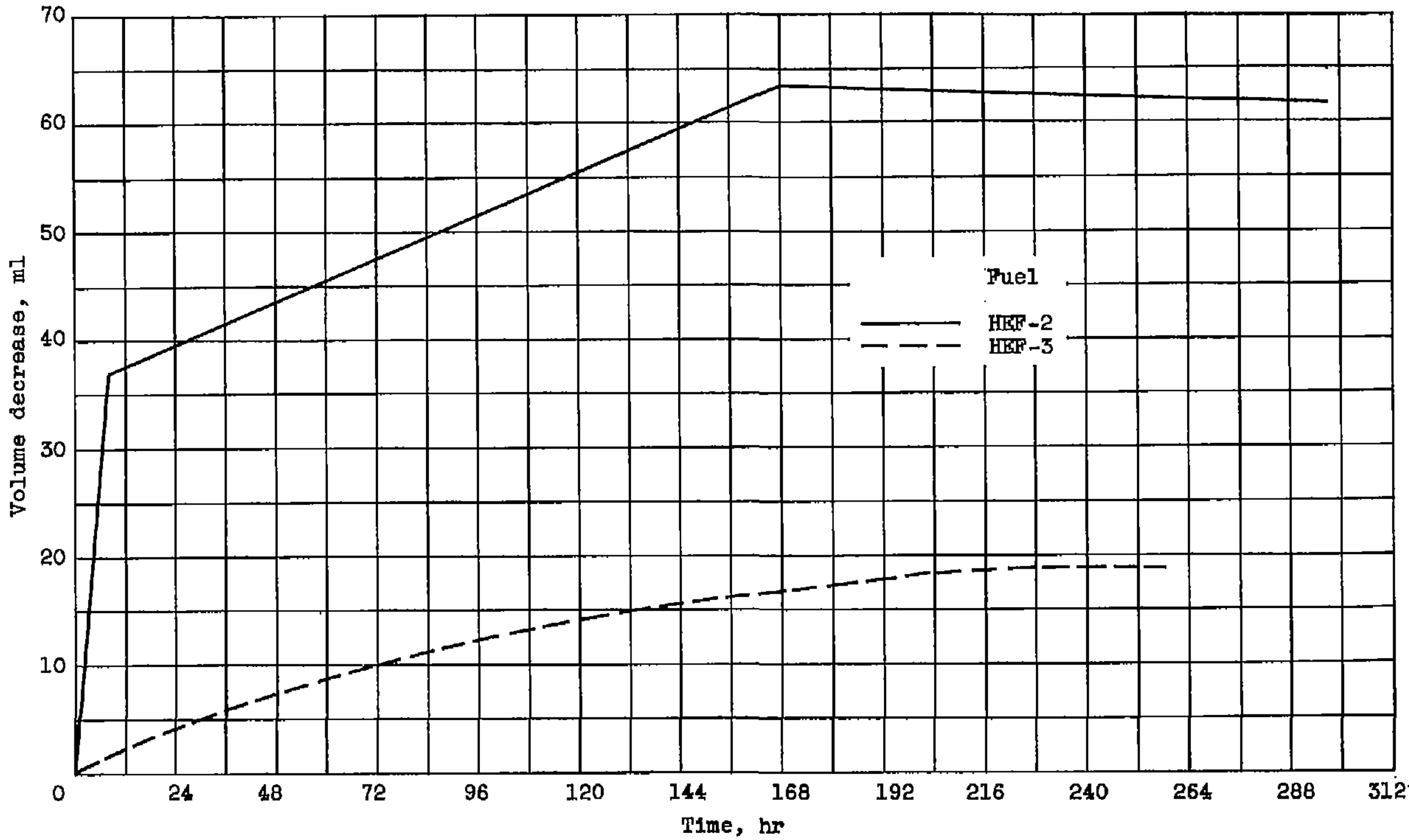

Figure 6. - Oxygen stability of HEF-2 and HEF-3.

4393

PHYSICAL AND CHEMICAL PROPERTIES OF HEF-2 (NACA FUEL 56Z4)

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